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THE VISCOSITY AND TENSILE PROPERTIES  
OF MIXED FIBER/BEAD REINFORCED  
PLASTICS

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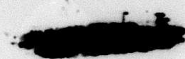
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An index of processability/mechanical properties trade-off is developed in order to determine the degree to which substitution of bead filler for fibers in fiber reinforced plastics might enhance processability without undue sacrifice of properties.

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## FOREWORD

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## INTRODUCTION

Fiber reinforced thermoplastics and thermosets exhibit many desirable properties in comparison to the base resin, including higher modulus, higher heat distortion temperature, and reduced mold shrinkage and warpage. However, fiber reinforced plastics are difficult to process by flow molding operations, due to increased viscosity in the melt or prepolymer and fiber breakage and segregation.

The trade literature contains references to improvement of processability by addition of particulate filler to fiber filled systems. However, no data exists to our knowledge on the processability or mechanical properties of well characterized, mixed-reinforced systems. Milewski (1) discussed the packing of mixtures of fibers and beads, but did not present properties data for reinforced systems.

In this paper we report initial investigations of the non-Newtonian viscosity of mixed suspensions of fibers and beads in viscous silicone oils, and of the mechanical properties of analogous composites of fibers and beads in polycarbonate resin. The total filler content is kept constant at 15 vol. %, and the proportion of filler which is beads is varied from 0 to 100%. Silicone oils were chosen as the matrix for viscosity measurements to avoid problems with high temperature rheometry and with resin and fiber degradation during mixing.

### Sample Preparation

Approximately 600g samples of suspensions of 30 $\mu$  diameter solid glass beads\* and nominal 1/8", 300  $\phi$ /d, chopped glass fibers\*\* in nominal 600 poise silicone oil\*\*\* were prepared by two techniques,

\* 3M Co.

\*\* Owens Corning

\*\*\* Dow Corning 200 Fluid



which were designed to cause low air entrapment and minimal fiber breakage at the mixing temperature of 25°C. Suspensions with fiber content of 6 vol. % and below were mixed at 3-5 rpm in a 2 l. reaction kettle under vacuum. The pure fluid was degassed, the appropriate amount of beads was added and dispersed, and then the fibers were added in small lots and mixed thoroughly between lots. Before mixing, the fibers were subjected to 400°C for 24 hr. to remove sizing. Suspensions with fiber content of 6 vol. % and above were prepared by kneading the components in an evacuated plastic bag. Suspensions with 6 vol. % fibers prepared by each method had essentially the same viscous properties.

The composites were prepared from the same fillers in the portion of rotomolding grade polycarbonate powder\* with particle size below 120 mesh. Random-in-a-plane composite preforms were made by a technique described in (2) which involves dispersing appropriate amounts of fibers, beads, and powder in a methanol/water solution, drawing off the fluid by vacuum filtration, and drying at 100°C for 24 hours under vacuum. Preforms were compression molded at 200°C and 6000 psi for 10 min. and water cooled. (3000 psi for pure polycarbonate). Dog bone tensile specimens were cut from each sample.

The compositions of both the suspensions and composites are shown in Table I.

Table I  
Composition of Composites and Suspensions  
(volume percent)

Sample No.	% Beads	% Fibers	% Matrix	Fiber/Bead Ratio
1	0	0	100	-
2	15	0	85	0.0
3	12	3	85	0.2
4	9	6	85	0.4
5	6	9	85	0.6
6	3	12	85	0.8
7	0	15	85	1.0

\* General Electric Lexan RP-700



### Experimental Procedure

Viscosity was measured at  $25 \pm 3^\circ\text{C}$  using a large bore capillary extrusion rheometer especially built in our laboratory for fiber suspension studies which is described in detail elsewhere (3). The rheometer barrel is mounted on a compression cell of an Instron testing machine and the piston is mounted on the crosshead. The barrel is 2 inches in diameter and 4 inches in depth and is fitted with a  $90^\circ$  entry cone. Dies with a diameter of  $1/4$  inch and lengths of one inch and seven inches were used. The apparent shear rates attainable with the device range from 2.6 to  $525 \text{ sec.}^{-1}$ .

True viscosity/shear-rate curves were obtained for the suspensions by applying first the Bagley end correction (4) and then the Rabinowitsch correction (5) to the raw data. Only two die lengths were used in calculating the end correction.

The tensile tests were conducted on an Instron testing machine equipped with a 1 inch extensometer. The testing speed was 0.05 in/min. Samples were tested at room temperature after drying in a vacuum oven at  $110^\circ\text{C}$  for 24 hours.

### Theories for Suspension Viscosity and Composite Modulus

Much effort has been devoted to prediction of the viscosity of concentrated suspensions over the years, and we will not review that work here. The only theories for the shear viscosity of concentrated fiber suspensions are those of Brodnyan (6) and Ziegel (7). No theories exist for the viscosity of mixed suspensions of fibers and spheres.

We explored several approaches to prediction of the modulus of a mixed fiber/bead composite; no attempt was made to predict the strength or breaking elongation of such systems. Consider first the approximate equation of Pagano and Tsai (8) for the tensile modulus of a random two dimensional short fiber reinforced composite:

$$E_c = 3/8 E_{11} + 5/8 E_{22} \quad (1)$$

$E_{11}$  and  $E_{22}$  are the longitudinal and transverse moduli of a unidirectional composite of the same material and composition and are given by the Halpin-Tsai equations (9).

For the mixed fiber/bead composites, eq. (1) was used to calculate the modulus of a composite containing only the fibers. This modulus was then used as the modulus of a pseudo-matrix in which the beads are the filler in the calculation of a tensile modulus using the Halpin-Tsai equations a second time. The resulting prediction is called here simply the prediction of the Halpin-Tsai equation.

Another approach was tried in which the Kerner equation (10) was used first to predict the modulus of a composite of the beads only. This value was employed as a pseudo-modulus with the fibers as filler in a Halpin-Tsai/Pagano-Tsai calculation. This prediction here is called Halpin-Tsai with Kerner.

A more empirical approach was also tried in which it was assumed that the modulus of a mixed composite is a linear function of the fraction of filler which is fibers, at constant total filler content. The end points of a straight line joining the moduli of a 15 vol. % bead and a 15 vol. % fiber composite were determined from the data, or on the fiber end by the Halpin-Tsai/Pagano-Tsai equations. The bead end was predicted using both the Kerner and the Smallwood (11) equations. The details of these calculations are given elsewhere (12).

## Results

The non-Newtonian viscosity curves for the mixed suspensions are shown in Fig. 1. Notice that the pure oil and the bead suspension are nearly Newtonian at shear rates up to  $200 \text{ sec.}^{-1}$ . In the same region the suspensions containing fibers are highly pseudoplastic, even at only 3 vol. % fibers/12 vol. % beads. The upward curvature of some of the curves suggests that a yield stress exists.

During extrusion none of these materials exhibited capillary die swell, but relatively large entrance corrections were observed. The end correction data are not displayed here, because they are confounded by an extra pressure drop due to rheometer friction. Fortunately, this error subtracts out in calculation of the viscosity. The fiber suspensions showed large rod-climbing or Weissenberg effects when mixed in the reaction kettle. A photograph is shown in (3) and (12).

The tensile moduli for the mixed composites are shown in Fig. 2, along with the predictions of the several theories. Each data point is the mean of six observations and the error bars represent one standard deviation. To a first approximation the modulus is a linear function of the fraction of filler which is fibers. The theoretical predictions, all of which are based on the Halpin-Tsai equations and eq. (1), are higher than the mean but within one standard deviation of the experimental observations for the composites containing fiber only. In addition, the Halpin-Tsai equations predict moduli which are higher than the data when employed over the entire relative concentration range. The Kerner and Smallwood equations agree quite well with the data for 15 vol. % beads, but as fibers are substituted for beads, the Halpin-Tsai equations pull the mixed theory values above the experimental



points. Optimized molding cycles might well give moduli higher than those observed here and more in line with the theoretical predictions.

The tensile strength and elongation of the mixed composites are shown in Fig. 3. Notice that the strength is a slowly increasing, essentially linear function of the fraction filler which is fibers. The elongation at break, however, falls off rapidly with the substitution of a small fraction of fibers for beads.

As an index of the trade-off between processability and mechanical properties of a composite, we chose the ratio of (suspension viscosity) to (composite modulus) as a function of the ratio of (vol. % fibers) to (vol. % solids). Since high modulus and low viscosity are generally desirable, low values of the trade-off index are deemed desirable. Of course, the index ratio is highly dependent upon the shear rate at which the viscosity is evaluated.

The values of the processability/property index are shown in Fig. 4. Notice that at the low shear rates characteristic of compression molding, the substitution of a small fraction of beads for fibers in a reinforced plastic reduces the viscosity proportionately more than the modulus; a good result. However, at high shear rates, more nearly characteristic of injection molding, the index ratio is insensitive to relative filler content, and one might as well retain all fibers to get maximum modulus enhancement.

Similar indices based on composite strength and elongation are included in (12). The trends are similar.

#### Discussion and Conclusions

Some initial data on the properties of mixed composites have been presented. It should be pointed out that neither the suspensions nor the composites have been optimized to obtain the best possible properties.



It is known, for example, that careful control of complex molding cycles is necessary to optimize reinforced polycarbonate. We purposely avoided use of polymer/filler interfacial agents which would enhance bonding and improve composite properties.

Recent work in our laboratory (13) demonstrates that the viscosity of concentrated fiber suspensions is sensitive to fiber length distribution and that fiber length in turn depends on the mixing conditions. The viscosities of the suspensions used in this study decrease upon repeated extrusion, indicating that equilibrium fiber length was not reached (13) during the mixing. Our objective in the work reported here was to retain the original fiber length as nearly as possible to make the suspensions comparable to the composites, in which few fibers were broken.

Milewski's work (1) suggests that we did not choose a good combination of bead and fiber sizes from the viewpoint of efficient packing; and that a different choice, probably smaller spheres, might lead to more striking improvements in viscosity upon the substitution of beads for fibers.

Clearly further work is needed to clarify the role of mixed spherical and fiber reinforcements in determining the processability and properties of polymer-based composites. Better systems might be chosen for investigation, and there may be more appropriate measures of processability than viscosity.

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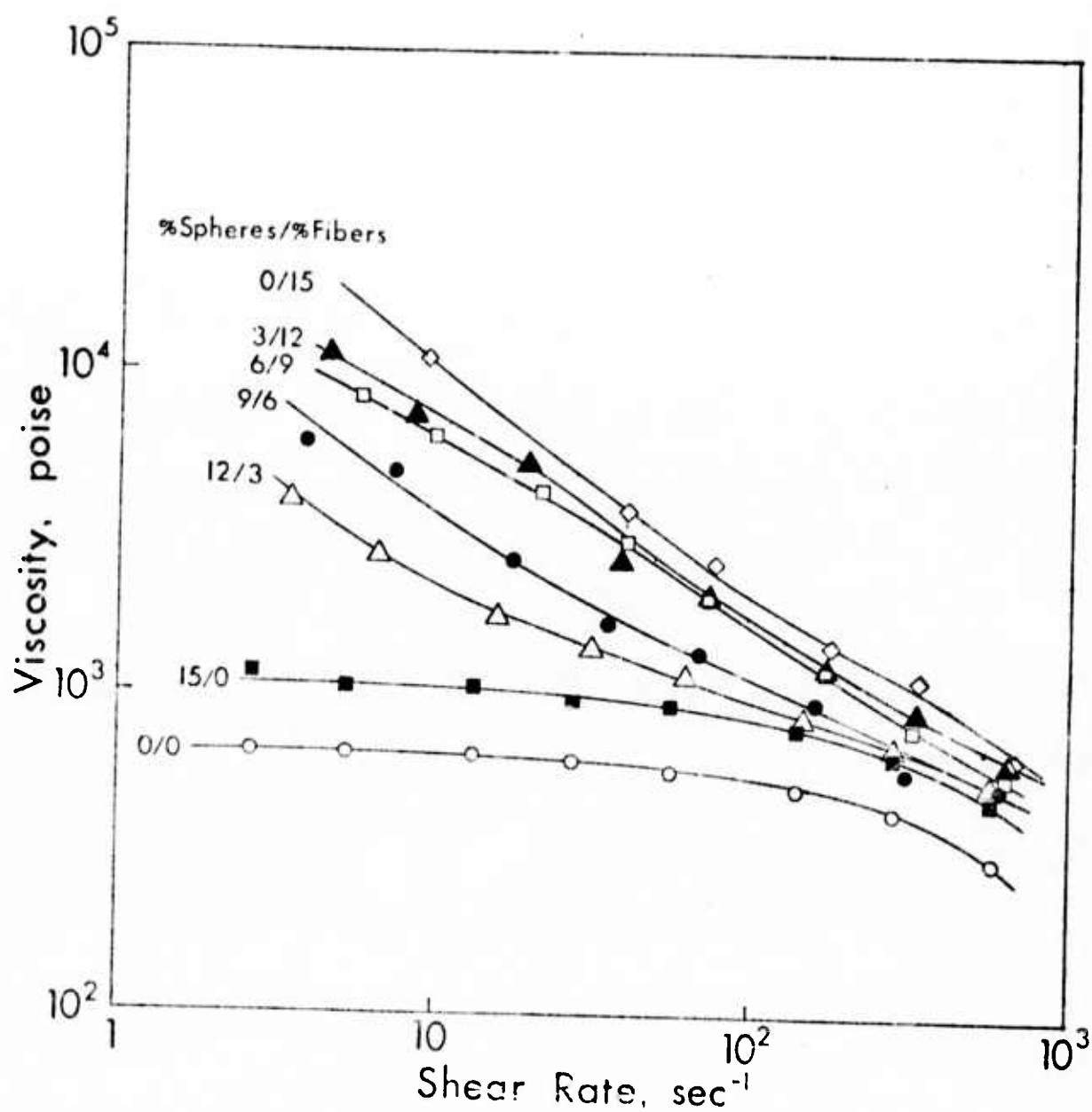


Figure 1 Viscosities of the Glass Sphere/Glass Fiber/Silicone Oil Suspensions

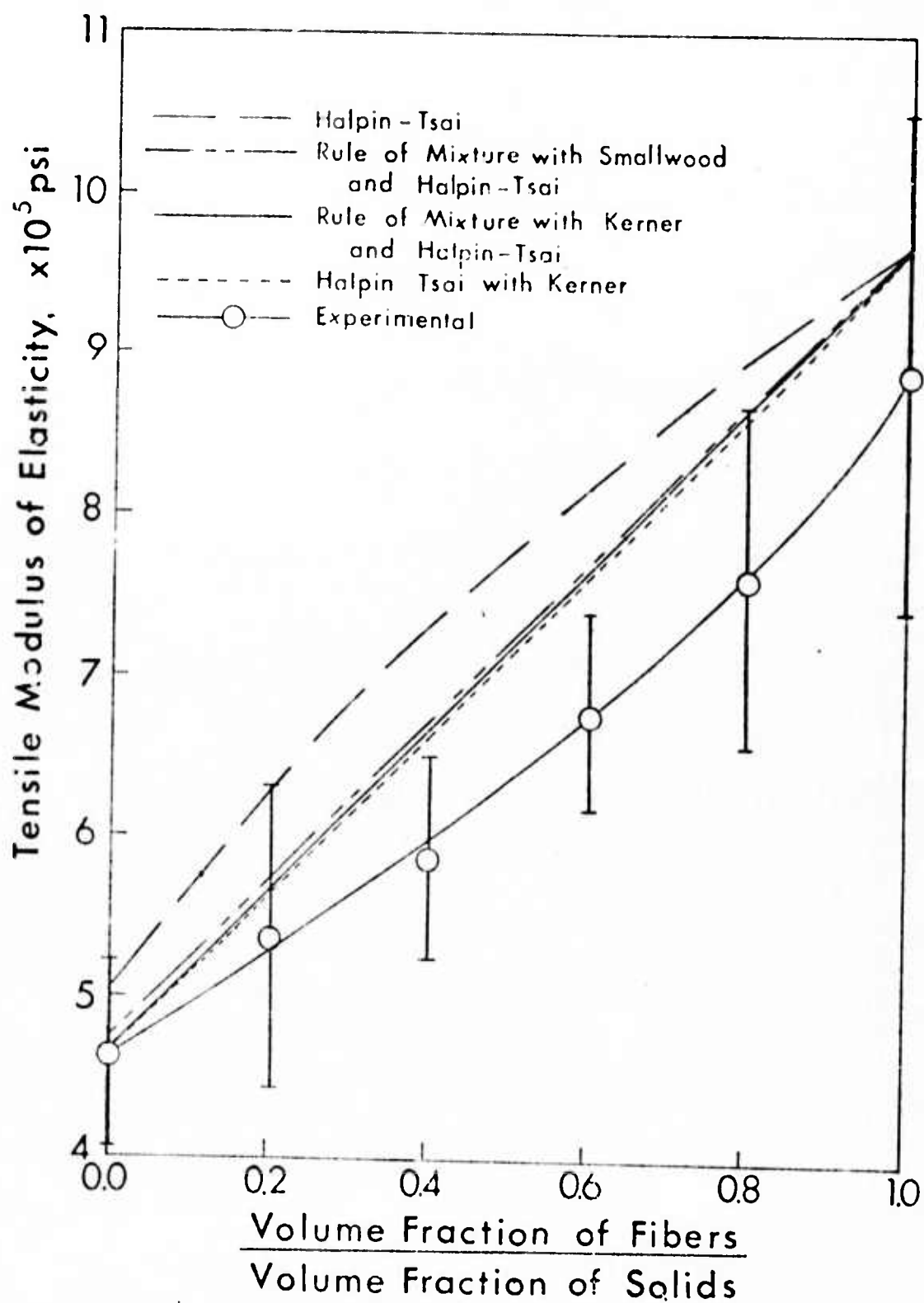


Figure 2 Comparison of Experimental and Theoretical Values of the Tensile Modulus



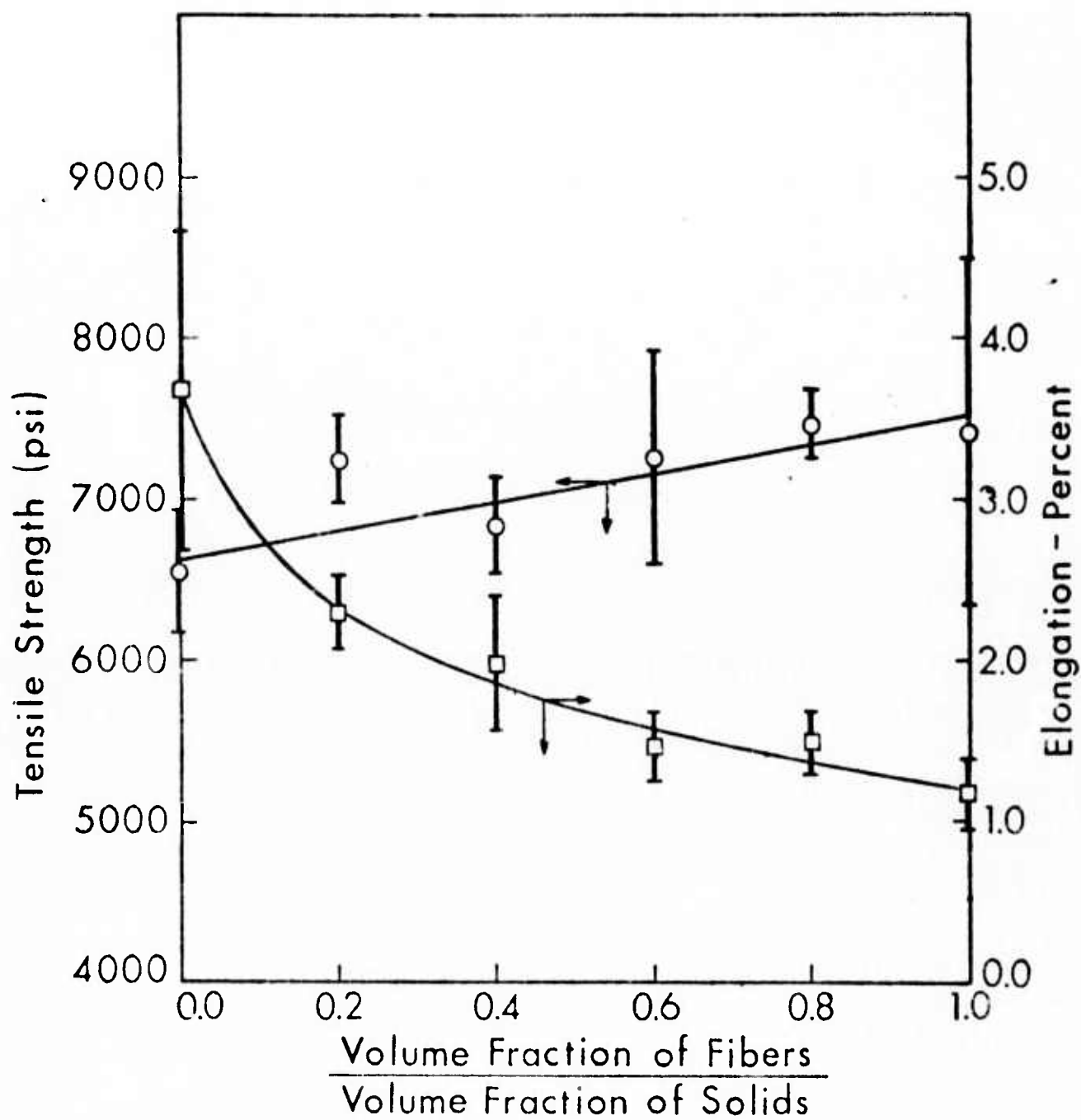


Figure 3 Strength and Elongation of the Fiber/Bead/Polycarbonate Composites

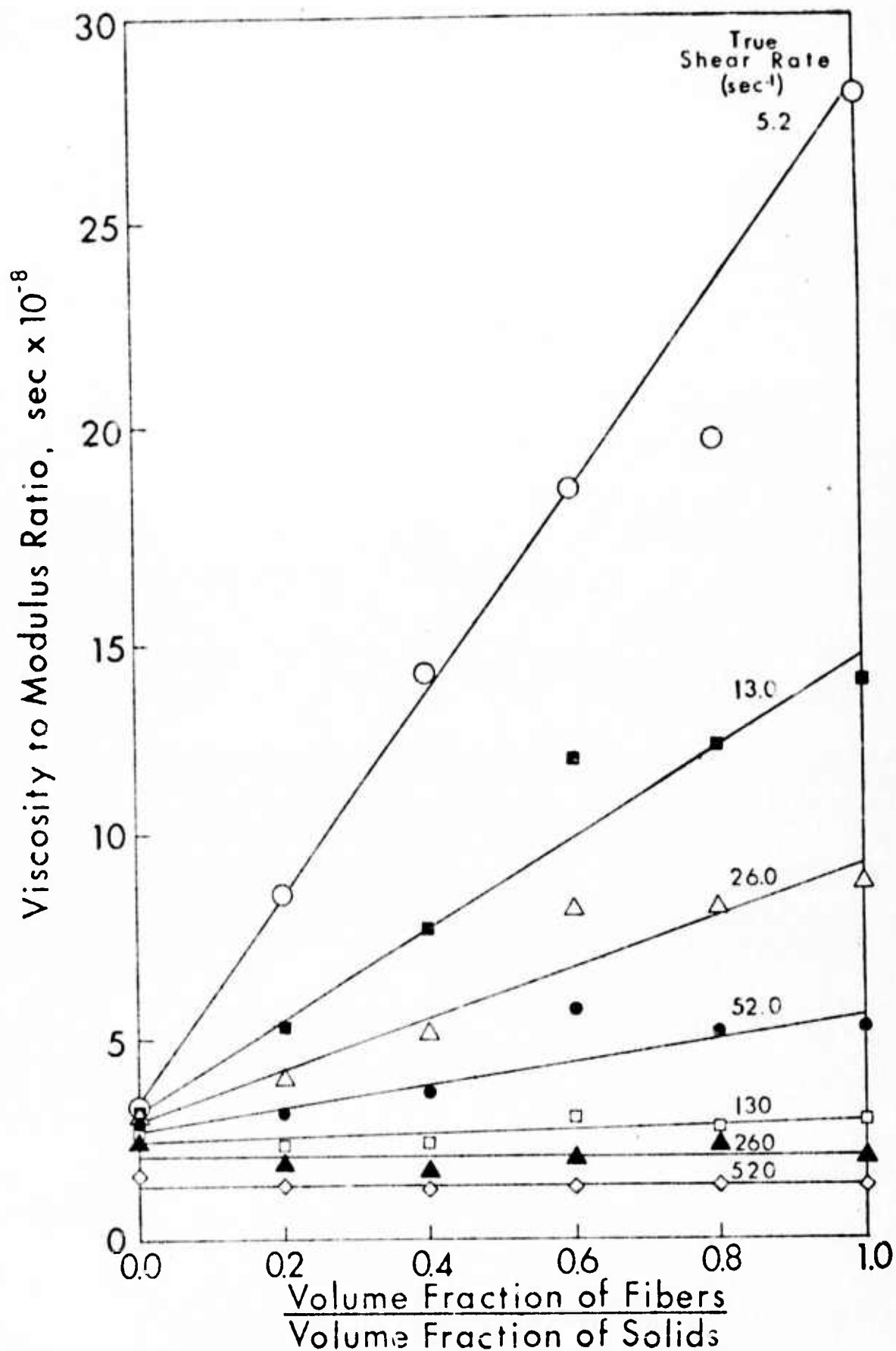


Figure 4 Processability/Mechanical Properties Trade-off Based on Viscosity and Tensile Modulus